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"NMR Study of Viscoelastic Fluids and Elastomers under Extreme  
Conditions of Temperature and Pressure"

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# TABLE OF CONTENTS

	<u>Page</u>
1. Abstract of Objectives and Accomplishments . . . . .	1
2. Viscous Fluids . . . . .	2
3. Ionic Mesophases . . . . .	9
4. Elastomers . . . . .	14
5. Instrumentation . . . . .	17
6. List of Publications . . . . .	18
7. Ph.D. Theses . . . . .	19
8. Research Personnel . . . . .	19

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## 1. Abstract of Objectives and Accomplishments

The project dealt with the investigation of the dynamic structure of three main disordered systems: i) viscous fluids, ii) ionic mesophases of melts of alkali metal carboxylates, and iii) selected polymer systems. The results obtained carried us towards our long term goal of better understanding the relationship between the molecular behavior and the macroscopic properties of the system studied. Our experiments on fluids help to bridge the current gap between molecular dynamics and hydrodynamics. In addition, considerable effort was devoted to the development of new instrumentation necessary for NMR experiments at extreme conditions of pressure and temperature.

In the case of viscous fluids, new insights have been gained concerning applicability of hydrodynamic equations at the molecular level. One of the objectives of this project was to provide a solid foundation for the systematic investigation of highly viscous fluids building on our experience and expertise in studies of low viscosity fluids. For several specific viscous fluids such as glycerol, di-(2-ethyl hexyl) phthalate, supercooled isopropylbenzenes we have carried out a detailed investigation of the molecular dynamics, interpreted our data in terms of available theoretical models and proposed new interpretations of specific aspects of the motional behavior.

In the studies of alkali metal carboxylates, our research efforts have focused on the dynamic structure of the mesophase and solid of sodium isovalerate and sodium n-butyrate. Our results in the liquid-crystalline ionic mesophase indicate that cation diffusion is very rapid and is independent of the rapid anion diffusion. Polarization microscopy experiments performed imply the ionic mesophase found in these melts consist of randomly oriented

domains of macroscopic dimensions having two-dimensional, smectic A (neat) structure. It is proposed that planes of diffusing ions affectively stabilize by electrostatic forces these unusual, long-lived mesophases. Results on solid sodium n-butyrate show the cation sublattice to be dynamically disordered. Analogies existing in the  $^{23}\text{Na}$  NMR data between the superionic conductor, sodium  $\beta$ -alumina, and solid sodium n-butyrate suggest solid sodium n-butyrate to resemble a fast ion conductor.

The exploratory experiments on elastomers dealt mainly with polybutadienes investigating various dynamic properties of elastomers under extreme conditions of high temperature and high pressure. A very useful information about the behavior of spin-spin relaxation times at high temperature in the motional narrowed region offers a possibility for diagnostic measure of the extent of crosslinking and/or presence of entanglements in polymeric systems investigated.

## 2. Viscoelastic Fluids

There have been numerous experimental and theoretical studies of motions in low viscosity ( $\sim 0.01$  P) organic fluids.

The dominant features of translational and reorientational diffusion coefficients, viscosity, and their variation as a function of temperature and pressure have been successfully attributed to the quickly varying repulsive intermolecular forces via two different approaches: (1) discrete molecular collisions as in a dilute gas corrected for excluded volume effects; and (2) hydrodynamics applied at the molecular level. The former approach is most successful over a time scale on the order of several molecular collisions whereas the latter is more successful

at including correlated motion effects which occur over a time scale of many collisions.

In contrast, fewer experimental and theoretical studies dealing with the molecular dynamics in viscous fluids ( $\eta > 1$  P) have been reported. There are several reasons for this lack of activity. Most liquids which may be made very viscous by supercooling or increasing pressure have a complicated molecular structure with many different conformations. This often necessitates gross assumptions about the molecular motions and their relation to the measured quantities. In principle, an anisotropic reorientation model allowing for internal rotations could provide a rigorous interpretation of experiments which probe molecular reorientation. However, for complicated structures, the number of parameters necessary to fit the model often greatly exceeds the number of independent measurements.

Additional complications arise which are associated with particular experimental techniques. Dielectric relaxation times,  $\tau_{\text{DIEL}}$ , and the correlation times derived from depolarized Rayleigh scattering,  $\tau_{\text{RAY}}$ , are both related to single particle reorientational correlation times by static and dynamic orientational pair correlation functions. These functions are not always easily determined.

Nuclear magnetic relaxation times can be clearly related to single particle correlation times. Other complications arise, however, when studying spin  $\frac{1}{2}$  nuclei such as protons. For such systems one must experimentally separate the inter- and intramolecular dipolar contributions to the relaxation rate or else make often unjustified assumptions of their relative contributions to the measured relaxation rate. Additionally, for viscous liquids, the relaxation rate may not be clearly associated with a particular

location on the molecule due to spin diffusion. Carbon-13 studies have the advantage that for carbons bonded to protons, the intramolecular dipolar relaxation rate usually dominates. The usefulness of conventional  $^{13}\text{C}$  NMR techniques is lost for fluids with viscosities much greater than 10 P. Two of these complications can be eliminated by measuring deuterium relaxation times. These are normally dominated by quadrupolar relaxation, thus providing information only about reorientational motions. Selective deuteration of a compound provides a probe of localized reorientational motions.

The theoretical explanations of molecular dynamics in viscous liquids are at a qualitative level partially due to the lack of experiments carried out under well defined conditions. The major physical explanations fall into two classes: those which are based on small step Brownian motion such as assumed for the Debye or Stokes-Einstein equations, or those which assume cooperative structural relaxation involving many molecules. The former has been successful for low viscosity fluids. The ability to vary the viscosity over many orders of magnitude in viscous fluids should provide an advantage over nonviscous fluids in testing the competing theories.

Our experiments on viscous fluids focused on several fundamental questions:

- 1) How are the motions at the molecular level and shear viscosity influenced by high pressure and temperature and how does molecular structure affect the relative volume and thermal effects?
- 2) To determine usefulness of hydrodynamic equations at the molecular level
- 3) To determine the applicability of various NMR relaxation techniques to study viscous fluids.
- 4) To test the various theoretical models proposed to describe the dynamic structure of viscous fluids, including supercooled fluids.



To highlight several specific results, we shall briefly describe several studies dealing with i) di(2-ethylhexyl)phthalate; ii) glycerol; and iii) isopropylbenzene.

i) Di-(2-ethylhexyl)phthalate Fluid.

The main purpose of our exploratory study of di(2-ethylhexyl)phthalate (DEHP) was to establish the usefulness of natural abundance  $^{13}\text{C}$  relaxation measurements for investigation of viscoelastic liquids. In addition, we wanted to find out whether the Debye equation can predict the reorientational correlation times as obtained from the natural abundance  $^{13}\text{C}$   $T_1$  data for individual carbons in DEHP even at viscosities in excess of 1 poise. Furthermore, the frequency dependence of the  $T_{1\rho}$  data enabled us to estimate the self-diffusion coefficients and to test the validity of the Stokes-Einstein equation at the molecular level for DEHP.

In summary, in all cases it was possible to describe the  $^{13}\text{C}$   $T_1$  behavior of individual carbon atoms by using the standard expression for  $T_1$  and calculating the approximate reorientational correlation times from the Debye equation. One does not require to invoke a distribution of correlation times to describe the  $^{13}\text{C}$  relaxation behavior in DEHP. It is quite clear that natural abundance  $^{13}\text{C}$  relaxation measurements appear very promising for studies of molecular motions in viscoelastic liquids.

The frequency dependence of the proton  $T_{1\rho}$  values in DEHP at lower temperatures ( $T \leq 273^\circ\text{K}$ ) was of particular interest. Since in the temperature range covered in our experiments one is still in the motional narrowing limit ( $\omega_1^2 \tau^2 \ll 1$ ) one makes the reasonable assumption that the  $T_{1\rho}$  dependence on  $\omega_1$  ( $\omega_1 = \gamma H_1$ ) arises from translational diffusion contribution to  $T_{1\rho}$  values. From expressions giving the frequency dependence of  $T_{1\rho}$ , one calculates self diffusion coefficients  $D_M$  and compares them with the value of  $D_S$ , the self-

diffusion coefficient obtained from the Stokes-Einstein equation. The good agreement between the  $D_M$  and  $D_S$  values can be regarded as further evidence that the Stokes-Einstein equation is valid even for viscosity values in excess of 1 poise.

ii) Glycerol Fluid

The pressure and temperature dependence of the deuteron NMR spin-lattice relaxation time  $T_1$  have been measured in liquid glycerol- $d_4$ ,  $(D_2COH)_2CHOH$ , and glycerol- $d_3$ ,  $C_3H_5(OD)_3$ , within the pressure range 1 bar to 5 kbar from  $-10^0$  to  $125^0C$ . The experimental deuteron relaxation data which reflect intramolecular reorientational motions were interpreted in terms of a Cole-Davidson distribution of correlation times. Within experimental error the distribution width  $\beta = 0.44$  was found to be independent of temperature and pressure. A single correlation time model and a model allowing for internal and overall reorientation failed to explain the experimental data without introducing an arbitrary adjustable parameter. The reorientational motions of the carbon backbone and of the hydroxyl groups are strongly correlated reflecting the effect of hydrogen bonds. By comparing the magnitudes of the  $T_1$  values at the minimum of the  $T_1$  vs  $T$  plots in glycerol- $d_4$  and glycerol- $d_3$  the deuteron quadrupole coupling constant was found to be 202 KHz for the hydroxyl deuteron. The dependence of the average correlation time  $\bar{\tau}_2$  upon viscosity and the  $\bar{\tau}_2$  variation with temperature and density was explained on the basis of a Debye type two term phenomenological equation. A discussion of the experimental data in terms of this equation suggested that the extent of the hydrogen bond network in liquid glycerol is relatively insensitive to density changes but very much reflects the temperature effects. The temperature and pressure dependence of the average

correlation time  $\bar{\tau}_2$  suggested that the reorientation of the glycerol molecule proceeds via a large-angle jump diffusion mechanism. A detailed comparison of the present results with the conclusions of other NMR studies was presented.

iii) Supercooled Isopropylbenzenes

In addition to the general objectives of our experiments on viscous fluids, as mentioned above, our systematic investigation of supercooled isopropylbenzene had the specific goal of elucidating the origin of the anomalous behavior of viscosity in the supercooled fluid state.

Since we realized that it is important to separate the intramolecular and intermolecular contributions to proton relaxation in isopropylbenzene, we performed the first isotropic dilution study in a supercooled - non-associative fluid.

Selectively deuterated samples of isopropylbenzene- $d_7$  (deuterated chain), isopropylbenzene- $d_5$  (deuterated ring), and perdeuterated isopropylbenzene were synthesized. The isopropylbenzene- $d_7$  proton spin-lattice relaxation times were measured at 60 MHz over a temperature range of  $-65^\circ$  to  $-132^\circ\text{C}$  at 0.25, 0.50, 0.75 and 1.0 mole fraction of isopropylbenzene- $d_7$  in perdeuterated isopropylbenzene. The relaxation rates were extrapolated to infinite dilution, with the intra and intermolecular contributions being separated using the method of Powles and Figgins.

In their studies of viscosity behavior of supercooled liquids, Barlow et al. (1966) have noted deviations from the Fulcher equation,

$$\ln \eta = A + B/(T - T_0) \quad (1)$$

where A, B, and  $T_0$  are constants. For some molecules, including isopropylbenzene, a discontinuity at the temperature  $T_k$  was found in their viscosity behavior. Below  $T_k$ , Eq. (1) fits the viscosity data with one set of constants,

whereas above  $T_k$ , a different set of constants must be used. For example, the  $T_k$  is  $171^\circ\text{K}$  for isopropylbenzene. This deviation was initially interpreted as a clustering phenomenon. A later paper by Davies and Matheson (1966), however, presented an analysis based on rotational motions, using the principles of the free volume theory. They described the transition from the high to the low temperature viscosity behavior as a complete quenching of free rotation. Thus, in the low temperature region, rotation could take place only as a result of translation. Since a translation step may or may not lead to a rotation step, the situation can be described by  $\tau_D \leq \tau_\theta$ ; where  $\tau_D$  is the diffusion correlation time and  $\tau_\theta$  is the reorientation correlation time.

Our experiments reveal several interesting features. First, the "discontinuity" temperature  $T_k$  is approximately at the minimum of  $T_1$  ( $\omega\tau \approx 1$ ), indicating motions occurring with a correlation time  $2 \times 10^{-9}$  sec. Secondly, and most significant, below  $T_k$  the intermolecular contribution to the ring proton relaxation rapidly decreases in comparison to the intramolecular contribution. Although the dependence of  $T_1$  on correlation time is mechanism dependent and the motions are anisotropic, we may safely assume that a separation of this magnitude reflects a real difference in the correlation times. Thus, at the lower temperatures,  $\tau_D > \tau_\theta$ . Indeed, the proton relaxation is very rapidly dominated by the intramolecular interaction. This appears to contradict the predicted behavior based on the viscosity results (i.e.  $\tau_D \leq \tau_\theta$ ).

In addition, the low temperature activation energies obtained by assuming a constant distribution parameter for the intra and isotropic jump diffusion for the inter (i.e. as shown in the correlation time plot)

are 5.2 kcal/mole and 18 kcal/mole respectively. It is interesting to make a qualitative observation that  $E_a$  (intra) and  $E_a$  (inter) compare favorably to the values of the activation energies for the  $\beta$  (5.7 kcal/mole) and (30 kcal/mole) relaxation as calculated from the dielectric data for isopropylbenzene as obtained by Johari and Goldstein (1970). This qualitative comparison indicates a possibility of a connection between the  $\beta$  relaxation and reorientational motions of the molecule. Additional viscous fluids such as methyl phthalate, sec-butylbenzene and their deuterium labelled analogues have been investigated. The theoretical interpretation of the experimental data is presently in progress.

### 3. Ionic Mesophases

#### 3.1. Liquid-Crystalline Melts

Short chain alkali-metal carboxylates in their molten states exhibit a number of unusual physical properties. Two members of this class of compounds, sodium isovalerate and sodium n-butyrate, form a mesophase at  $T_F = 188^\circ\text{C}$  and  $T_F = 252^\circ\text{C}$ , respectively. It has been proposed that this mesophase consists of randomly oriented smectic domains. At  $T_{CL} = 280^\circ\text{C}$  and  $T_{CL} = 324^\circ\text{C}$ , respectively, the mesophase undergoes a transition into an isotropic melt. In addition to being possible model mesogens for lamellar lyotropic liquid crystals such as biological membranes, these compounds exhibit some properties typical of two-dimensional fast ion conductors, specifically sodium  $\beta$ -alumina.

Previous work of our group (Wolfe, Bonekamp and Jonas, 1979) has shown anion diffusion within the layers of the domains of the sodium isovalerate mesophase to be very rapid ( $D \sim 5 \times 10^{-7} \text{ cm}^2/\text{sec}$ ) while domain-domain interactions are manifested through macroscopic properties such as the

estimated shear-rate dependent viscosity ( $\sim 100\text{P}$ ). More recently, we have found similar anion diffusion behavior in the mesophase of sodium n-butyrate.

On the basis of their thermodynamic measurements for both fusion and clearing transitions and because of the high conductivity ( $\sigma \sim 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ ) observed in the mesophase of sodium isovalerate, Ubbelohde, et al. (1970) suggested an occurrence of separate positional melting of cation and anion lattices. Our present NMR study of sodium in these materials was motivated by the observation of a rapid anion diffusion in sodium isovalerate and by the success of  $^{23}\text{Na}$  NMR experiments in fast ionic conductors and in a variety of organic and bioorganic systems.

To our best knowledge, we report the first observation of a second order quadrupole effect for  $^{23}\text{Na}$  in any liquid crystal. Indeed this appears to be the first  $^{23}\text{Na}$  NMR study in anhydrous liquid crystals (thermotropic). The presence of such strong quadrupole effects coupled with rapid anion and cation diffusion suggests that these mesophases have "sandwich-type" domain structure stabilized by electrostatic forces (charge planes) rather than a large molecular length-to-width ratio ( $> 4$ ) normally considered essential for liquid crystalline phase formation.

Sodium isovalerate and sodium n-butyrate samples were prepared in a manner previously described. The  $^{23}\text{Na}$  lineshapes in each compound were recorded at 47.6 MHz by the Fourier transform method using an Oxford Instrument superconducting magnet operating at a field of 42.2 kG.

It is important that in spite of the rapid  $\text{Na}^+$  motion present in the mesophase we observed a second order quadrupole effect for the central transition. In this regard, our system resembles sodium  $\beta$ -alumina which also has rapid cation diffusion ( $\tau_c \sim 5 \times 10^{-9}$  sec at room temperature) and non-averaged quadrupole effects. Recently the  $^{23}\text{Na}$  NMR data for sodium

$\beta$ -alumina has been successfully described using a two-dimensional continuum diffusion model, where on an NMR time scale, the cation motion is liquid-like. In the framework of this model which involves a time dependent perturbation treatment, the quadrupole effects on the lineshape do not average out for the two-dimensional diffusive motion. In the fast-motion regime ( $\omega_L \tau_C \ll 1$ ) and for the effective asymmetry parameter equal zero the expression for the second order quadrupole shift reduces to the well known expression given by Cohen and Reif (1957) for the second order quadrupole shift in solids for the case,  $\eta = 0$ . In this model, it can be shown that an effective axially symmetric field gradient may be the result of rapid motion. In view of the smectic structure and the rapid anion and cation anisotropic diffusion, a two-dimensional liquid model appears to be a viable description of our experimental data.

### 3.2. NMR Experiments on the Solid State

Recent experiments on the solid phases of sodium isovalerate and sodium *n*-butyrate have been performed in an attempt to characterize the motions of the cation. As thermodynamic measurements indicate the possibility of separate positional melting, we have explored particularly this possibility in the solids of both carboxylate salts. Our results indicate that the cation sublattice is dynamically disordered in the solid. Most notable are the similarities existing in the  $^{23}\text{Na}$  NMR data between sodium *n*-butyrate and the superionic conductor, sodium  $\beta$ -alumina.

We have intensively investigated the  $^{23}\text{Na}$  NMR of both sodium isovalerate and sodium *n*-butyrate in their polycrystalline form from  $T_f$  to  $-70^\circ\text{C}$ . Since the  $^{23}\text{Na}$  nucleus has a nuclear quadrupole moment the effect of quadrupolar interaction is important. The Fourier transform spectra obtained

show the presence of both the dipolar interaction and the quadrupolar interaction. Spin-lattice relaxation,  $T_1$ , was also studied throughout the solids.

The powder pattern of the second order quadrupolar shift was obtained via Fourier transform spectroscopy for the central transition ( $m = -1/2 \leftrightarrow +1/2$ ). It is noteworthy that the first order quadrupole splittings could not be obtained in the solid due to quadrupolar broadening. The splittings can not be directly obtained in conventional Fourier transform spectroscopy in sodium  $\beta$ -alumina as well. Although work is still in progress to determine more accurately the temperature dependence of the quadrupole coupling constant,  $Q_{cc}$ , and of the asymmetry parameter,  $\eta$ , the value of the  $Q_{cc}$  has upper limits of 1.85 and 1.25 MHz for solid sodium isovalerate and sodium n-butyrate, respectively. That these values are near, but less than the  $Q_{cc}$  for sodium  $\beta$ -alumina ( $Q_{cc} \sim 2\text{MHz}$ ) is of importance.

Linewidth data is dominated by dipolar broadening at least in sodium n-butyrate solid I and II and in solid sodium isovalerate near  $T_F$ . The gradual narrowing of the dipolar linewidth and the failure to attain a rigid lattice value are two additional features of our data for sodium n-butyrate which are in common with sodium  $\beta$ -alumina. From the narrowing regions a correlation time,  $\tau_d$ , for the  $\text{Na}^+$  motions may be obtained. That this motion is fast cation diffusion rather than localized jumping is indicated by the fairly high conductivity ( $\gamma \sim 5 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ ) observed for solid sodium isovalerate near  $T_F$ .

Quadrupolar relaxation dominates the spin-lattice relaxation,  $T_1$ , throughout the solid. Interestingly,  $T_1$  minima are observed at  $T_F$  in sodium isovalerate and very near  $T_F$  in solid I of sodium n-butyrate. As predicted by Hubbard and observed for sodium  $\beta$ -alumina,  $T_1$  is non-exponential in the



motionally slowed regime ( $\omega_0 \tau_c \gg 1$ ). The degree of non-exponentiality is much more complicated in the sodium carboxylate solids and in high crystal sodium  $\beta$ -alumina than that predicted by Hubbard using simple BPP spectral densities. A promising explanation of our  $T_1$  data utilizes a two-dimensional-continuum diffusion model.

Using  $T_1$  data, a correlation time,  $\tau_c$ , for electric field gradient fluctuations may be found. As has been obtained for sodium  $\beta$ -alumina, a disparity in values but agreement in activation energies exists between  $\tau_c$  and  $\tau_d$ . This implies long-range diffusive motion of  $\text{Na}^+$  ions dominates the nuclear spin relaxation throughout much of the sodium n-butyrate solid and the sodium isovalerate solid near  $T_F$ . It should be pointed out that anomalies in the prefactor for  $\tau_d$  have been observed for many types of superionic conductors, sodium  $\beta$ -alumina included.

Our experiments and analyses lead us to conclude that there is considerable disorder in the solid. Our results for sodium n-butyrate are particularly interesting. Not only does the anion sub-lattice appear to be orientationally disordered prior to  $T_F$ , but also the cation sub-lattice appears to be dynamically disordered as early as  $T_{III,II}$ . Importantly, the  $\text{Na}^+$  in diffusive motion appears to be long-range. In view of the numerous similarities existing between sodium n-butyrate and sodium  $\beta$ -alumina, the possibility that solid I and II sodium n-butyrate has two-dimensional or channel structure is quite high. Although pending confirmation via further experiments in conductivity, some of the sodium carboxylates appear to behave as fast ion conductors in their solid state.

#### 4. Elastomers

The field of polymers represents a new area of investigation for our research group. The objective of a number of initial experiments was not only to solve several specific problems but to help us to orient ourselves in this field. In our earlier studies (Munie, Jonas and Rowland 1980) we investigated the effects of crosslinking at the molecular level, i.e. the permanent network formation. In this specific study, we found that the spin-spin relaxation times,  $T_2$ , and the free reduction decay per sec are very sensitive to network formation and are well suited for characterization of chemically crosslinked samples.

As a continuation of our research program, we have investigated the effects of molecular entanglements i.e., transient network formation, on the behavior of well characterized samples of polybutadiene (Munie and Jonas, in preparation).

Proton relaxation measurements have been used to investigate the effect of entanglements on segmental motion in polybutadiene samples of narrow molecular weight distribution. The temperature and pressure dependencies of the proton spin-lattice relaxation time,  $T_1$ , the proton spin-spin relaxation time,  $T_2$ , and the spin-lattice relaxation time in the rotating coordinate frame,  $T_{1\rho}$ , were reported. Use of these various relaxation times allows us to probe frequencies of molecular motions from very low frequencies to the MHz region. The three polybutadiene samples have weight average molecular weights of 2,700, 17,00, and 423,000. These values are below to well above the reported values of molecular weight for entanglements. The relaxation data are interpreted in terms of the effects of entanglements on segmental chain motion. Because of their sensitivity to low frequency

motions, the  $T_2$  data are of special interest. At temperatures above the  $T_1$  minimum, the small  $T_2$  temperature dependence reported earlier for crosslink samples is found only in the highest molecular weight sample. This solid-like behavior of  $T_2$  reflects the non-zero averaging of dipolar interactions due to anisotropic motion of the chain segments between entanglement. There is a correlation between the proton  $T_2$  values and the number average molecular weight.

In an earlier study (Liu and Jonas 1975) of several elastomers, we found that the activation volume  $\Delta V^\ddagger$  exhibits a strong temperature dependence - the  $\Delta V^\ddagger$  for  $T_1$  was found to increase with increasing temperature in contrast to the opposite trend in  $\Delta V^\ddagger$  with temperature observed in viscoelastic measurements and dielectric relaxation measurements. In our study of polybutadienes we were able to provide an explanation for this observation. The activation volume  $\Delta V^\ddagger$  for the various relaxation processes have been calculated and we found that  $\Delta V^\ddagger$  for  $T_1$  increases with temperature whereas  $\Delta V^\ddagger$ 's for  $T_2$  and  $T_{1\rho}$  are found to decrease with temperature in agreement with reported  $\Delta V^\ddagger$  values obtained for viscoelastic and dielectric measurements. The reason why the temperature behavior of  $\Delta V^\ddagger$  for  $T_1$  is different from that obtained for  $T_2$ ,  $T_{1\rho}$ , viscoelastic and dielectric relaxation measurements, is related to the fact that  $T_1$  is determined by high frequency localized chain motions whereas the other relaxation parameters reflect low frequency motions; i.e. motions of large segments of polymers.

In order to obtain more information about techniques for our specific studies of elastomers, detailed measurements of the spin-echo  $\ln A$  vs.  $\tau$  curve were made in the temperature range 25 to 145°C on samples of mono-disperse peroxide crosslinked polybutadiene of known crosslink density

(Brown and Jonas, unpublished results). Starting materials of two different molecular weights greater than the critical entanglement weight were cross-linked in solution and in bulk. Each network was studied with entangled sol molecules present and with the sol extracted.

As observed leveling off in the high temperature  $T_2$  values is in agreement with previously observed behavior in polybutadiene melts. This "pseudosolid plateau" is attributed to nonzero motional averaging of the dipolar coupling.

The presence of the entangled sol molecules was determined by comparison of the spin-echo  $\ln A$  vs.  $\tau$  curves of unextracted and extracted samples. In the unextracted samples, the more mobile sol component extended the signal to longer  $\tau$  values. The  $\ln A$  vs.  $\tau$  curves were unexponential but contrary to results in polydimethylsiloxane and cis-polyisoprene the relative amounts of sol and gel fraction did not separate quantitatively.

Extracted samples also showed nonexponential decay. The chemical extraction process which removed the sol molecules must have in the case of high sol fraction caused a large change in the morphology of the network. However, the spin-echo curve for the extracted samples still showed both a fast and slow spin-spin relaxation process, little changed from the unextracted samples except for a small decrease in  $T_2$ . The lower molecular weight sample showed the least change after sol extraction. This could be interpreted as new NMR evidence for damage healing as network chains diffuse and entangle to fill microvoids formed by the extraction process.

Our exploratory, unpublished NMR experiments on samples on fluoro-silicone sealants obtained from Mr. Warren Griffin, Fluids, Lubricants, and Elastomer Branch, AFML-MBT, Wright-Patterson AFB, have yielded the following results:

- 1) The proton  $T_2$  measurements and a detailed investigation of proton and fluorine free induction decays indicate the effects of non-zero averaging of dipolar interactions due to anisotropic motions of the chain segments at high temperatures in the motionally narrowed region.
- 2) The measurements of  $^{13}\text{C}$  spectra at natural abundance and of  $^{29}\text{Si}$  spectra confirmed that the high resolution spectroscopy at high magnetic fields has a great promise as an analytical tool to study fluorosilicone sealants.
- 3) The  $^{13}\text{C}$  experiments showed that in the motionally narrowed region, the fluorosilicone polymers can be studied by using the standard  $^{13}\text{C}$  high resolution techniques without the need of the multiple pulse techniques.

#### 5. Instrumentation

Acquisition of a wide-bore, high field superconducting magnet (funded by the NSF) allowed us to build a new NMR spectrometer system which is being presently used in our research supported by the AFOSR. Major instrumentation effort was required to design and build a high pressure NMR probe which enables us to high resolution NMR spectroscopy at extreme conditions. We have successfully developed a NMR probe which is unique in its performance features such as: i) wide pressure and temperature range; ii) high resolution, i.e., at 180 MHz linewidth 1-2 Hz for 10 mm sample diameter; iii) large sample volume; iv) reliable high-pressure RF feedthroughs; v) contamination-free sample cell; vi) suitability for superconducting magnets. We would like to emphasize that our current experimental capabilities are unique. We can do high resolution NMR spectroscopy using Fourier Transform approach on samples under high pressures. According to our best knowledge there is no NMR spectrometer with comparable performance features in the U.S.A.

and/or abroad. The design and building of a high pressure viscometer, which enables viscosity measurements in the range  $10^{-2}$  poise to  $10^7$  poise, represented another instrumentation effort supported by the AFOSR.

6. List of Publications Acknowledging AFOSR Support

1. "Density and Temperature Effects on Some Transport Properties of Perfluorocyclobutane," R. J. Finney, M. Fury and J. Jonas, J. Chem. Phys., 66, 760 (1977).
2. "NMR Study of Angular Momentum Relaxation in Fluids. I. Compressed  $CF_4$ ," R. J. Finney, M. Wolfe, and J. Jonas, J. Chem. Phys., 67, 4004 (1977).
3. "NMR Study of Angular Momentum Relaxation in Fluids. II. Mixtures of  $CF_4$  with Inert Gases," M. Wolfe, E. Arndt, and J. Jonas, J. Chem. Phys., 67, 4012 (1977).
4. "Magnetic Resonance Spectroscopy at High Pressure," J. Jonas, Proceedings NATO ASI, High Pressure Chemistry, held at Corfu, Greece, 1977, p. 65-110 (D. Reidel Publ. Co., Dordrecht, Holland, 1978).
5. " $^{13}C$  and  $^1H$  Relaxation in Viscous Liquid of Di-(2-Ethylhexyl) Phthalate," J. Jonas and E. Arndt, J. Magn. Resonance, 32, 297-301 (1978).
6. "Transport and Relaxation in Mesophase of Organic Salt Melt," M. Wolfe, J. Bonekamp and J. Jonas, J. Chem. Phys., 70, 3993-3994 (1979).
7. "Reorientational Motions in Compressed Viscous Fluids: Selectively Deuterated Glycerol," M. Wolfe and J. Jonas, J. Chem. Phys. 71, 3252 (1979).
8. "Molecular Motions in Dense Liquids," J. Jonas, Proceedings Joint ACS and JCS Meeting, Hawaii, April, 1979 Nanko-do Publ. Tokyo, Japan 1979, Kagaku No Ryoiki, 33, 987-995 (1979).
9. "NMR in Chemistry - An Evergreen," J. Jonas and H. S. Gutowsky, Prefatory Chapter, Ann. Rev. Phys. Chem., 31, 1-27 (1980).
10. " $^{23}Na$  NMR Study of Ionic Mesophases of Molten Sodium Carboxylates" J. Bonekamp, T. Eguchi and J. Jonas, Chem. Phys. Lett., 75, 360 (1980).
11. "High Resolution Probe for NMR Measurements at High Pressures and High Fields", J. Jonas, D. L. Hasha, W. J. Lamb, G. A. Hoffman, T. Eguchi, J. Magn. Resonance 42, Jan. issue (1981).
12. "Nuclear Magnetic Resonance Studies at High Pressures", J. Jonas, Rev. Phys. Chem. JAPAN, 50, 0000 (1980).

13. " $^1\text{H}$  and  $^2\text{D}$  NMR Study of Isopropylbenzene Ring Motions in the Supercooled Liquid State", E. Arndt and J. Jonas, J. Phys. Chem. submitted.
14. "NMR Solid State Study of Alkali Metal Carboxylates", J. Bonekamp, T. Eguchi and J. Jonas, Manuscript in Preparation.
15. "NMR Study of Entanglement Effects in Polybutadienes", G. C. Munie, D. Brown and J. Jonas, Manuscript in Preparation.

7. Ph.D. Theses

Dr. Michael Stephen Wolfe

"High Pressure Nuclear Magnetic Relaxation Time Studies of Collision-Limited and Structure-Limited Fluids", University of Illinois, Urbana, Ill., 1979.

8. Research Personnel:

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